

EFFECT OF SULFOMETURON METHYL ON GROUND WATER AND STREAM QUALITY IN COASTAL PLAIN FOREST WATERSHEDS¹

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ABSTRACT: Sulfometuron methyl [methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate] was applied by a ground sprayer at a maximum labeled rate of 0.42 kg ha⁻¹ a.i. to a 4 ha Coastal Plain flatwoods watershed as site preparation for tree planting. Herbicide residues were detected in streamflow for only seven days after treatment and did not exceed 7 mg m⁻³. Sulfometuron methyl was not detected in any stormflow and was not found in any sediment (both bedload and suspended). Sampling of a shallow ground water aquifer, < 1.5 m below ground surface, did not detect any sulfometuron methyl residues for 203 days after herbicide application. Lack of herbicide residue movement was attributed to low application rates, rapid hydrolysis in acidic soils and water, and dilution in streamflow.

(KEY TERMS: sulfometuron methyl; herbicide; ground water; water quality; slash pine; environmental fate.)

INTRODUCTION

One aspect of intensive southern pine management that is receiving much attention is herbaceous weed control in very young plantations. Early herbaceous competition control results in significant increases in seedling height and diameter over untreated seedlings (Michael, 1985). Hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine 2,4(1H,3H)-dione], atrazine (2-chloro-4-ethylamino-6-isopropylamino-5-triazine), and simazine [2-chloro-4,6-bis(ethylamino)-s-triazine] produce beneficial but variable results when used to release loblolly pine from herbaceous competition (Fitzgerald, 1976; Nelson, *et al.*, 1981).

Sulfometuron methyl [methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate] controls a broad range of herbaceous species and is exceptionally safe for application to pine seedlings (Atkins, 1986; Knowe, 1984; Michael, 1983; Nelson, *et al.*, 1984). This herbicide produces good early pine

growth without the adverse effect of pine mortality often associated with other release chemicals (Clason, 1984; Michael 1985; Neary, *et al.*, 1984). Like most forestry herbicides developed since the suspension of 2,4,5-T [(2,4,5-trichlorophenoxyacetic acid)], sulfometuron methyl is effective at very low rates. Thus, its use is likely to increase significantly by replacing or supplementing other site preparation and release chemicals.

An increase in the use of herbicides in forest management has heightened public concerns over possible adverse environmental impacts, particularly to surface waters and ground water. Development of forestry herbicides in recent years has focused on production of chemicals which are less persistent, more effective at low rates, and low in toxicity to non-target organisms. The degree to which applied forestry pesticides persist in or move off-site in water is dependent on the application method, soil physical and chemical properties, site characteristics, timing of application, weather, and the properties of the applied chemical (Norris, 1981).

Herbicide fate in forest ecosystems has not been studied as extensively as in agricultural ecosystems (Wauchope, 1978; Wauchope and Leonard, 1980), particularly for the newer chemicals. Much of the information available for the phenoxy herbicides such as 2,4-D [2,4-dichlorophenoxy) acetic acid] and 2,4-DP [(2,4-dichlorophenoxypropionic acid] has been summarized by Norris (1981). From applications of 1-2 kg ha⁻¹, runoff concentrations are reported to vary from nondetectable to a maximum of 825 mg m⁻³. Studies of the offsite movement of hexazinone from applications of 1-2 kg ha⁻¹ show peak runoff concentrations in permanent streams ranging from nondetectable (Neary, 1983) or trace (Neary, *et al.*, 1985a) to 442 mg

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m^{-3} (Neary, *et al.*, 1983) to $2,400 \text{ mg m}^{-3}$ (Miller and Bace, 1980).

Picloram (4-amino-3,5,6-trichloro-2-pyridine carboxylic acid) has been reported to move off-site in streamflow from applications of $5.6 \text{ kg a.i. ha}^{-1}$ peak streamflow concentrations ranged from 10 mg m^{-3} in the mountains of North Carolina (Neary, *et al.*, 1985b) to 241 mg m^{-3} at a site in central Alabama (Michael, *et al.*, 1989).

Movement of herbicides through the soil profile is used as an indication of the potential for leaching into ground water. The site variables involved are sufficiently different to negate any simple relationship between soil concentrations and ground water contamination. Application of approximately 1.6 kg ha^{-1} of hexazinone to an upper Piedmont site resulted in a maximum observed soil solution concentration for the upper 30 cm of 108 mg m^{-3} with a maximum stream baseflow concentration of 20 mg m^{-3} (Neary, *et al.*, 1983). In another study, hexazinone was detected at a depth of 1.0 m at a maximum concentration of 241 mg m^{-3} in soil solution following application of 1.6 ha^{-1} for site preparation in Michigan. However, no detectable residues were found in stream flow from the treated site (Neary, *et al.*, 1985a). Picloram detected in soil solution at a depth of nearly 60 cm (concentration of 381 mg m^{-3}) was followed by a maximum stream concentration of 10 mg m^{-3} (Neary, *et al.*, 1985b). On an Upper Coastal Plain site, maximum soil solution concentrations of 400 mg m^{-3} at 30 cm in depth resulted in streamflow concentrations of 242 mg m^{-3} (Michael, *et al.*, 1989).

There are no published data concerning the fate of sulfometuron methyl in forest ecosystems. Available toxicology data ($\text{LD}_{50} > 5,000 \text{ mg kg}^{-1}$ and 96 hour LC_{50} for bluegill sunfish (*Macrochirus lepromis*) $12,500 \text{ mg m}^{-3}$) indicate it is almost nontoxic to animals and fish and is not considered to be a mutagen or teratogen (DuPont, 1984). The impacts of sulfometuron methyl on some aquatic plant species has also been studied (USDA ARS, 1982). Growth of *Cladophora* spp., a filamentous alga, was not reduced by exposure to $5,000 \text{ mg m}^{-3}$ of sulfometuron methyl. Hydrilla (*Hydrilla verticillata* Royle), a submerged aquatic plant, was not affected by exposure to 50 mg m^{-3} of the herbicide, but exposure to 100 mg m^{-3} resulted in a significant reduction in growth. Growth of Eurasian watermilfoil (*Myriophyllum spicatum* L.) was reduced at water concentrations of 1 mg m^{-3} . Clearly, susceptibility for aquatic species varies, just as it does for terrestrial species.

Sulfometuron methyl is relatively insoluble in water (10 mg L^{-1}) at pH 5.5, and is unstable in acid aqueous solution with a hydrolytic half-life of approximately 14 days at pH of 4.5 (> 40 days at pH 7). Sulfometuron methyl with its low solubility and low

partition coefficient ($K_d = 0.29$; Dickens and Wehtje, 1986) would be available for washoff unless its leaching from or degradation in the upper centimeter of soil is rapid. The instability of sulfometuron methyl in aqueous phase in acid forest soils may reduce its potential to move off-site. Thin layer chromatograph studies of sulfometuron methyl movement in agricultural soils of Alabama ($R_f = 0.86$; Dickens and Wehtje, 1986) have indicated considerable mobility potential for this herbicide.

The objectives of this study were to evaluate sulfometuron methyl off-site movement in streamflow, with sediment transport, and by leaching into ground water on a typical Lower Coastal Plain flatwoods site.

METHODS

Site Description

The study site, which is located on Container Corporation of America land, is in Alachua County 10 km north of Gainesville, Florida, in typical flatwoods terrain. Soils are acid (pH 4.0) and somewhat poorly drained Spodosols (sandy, siliceous, hyperthermic Typic Haplaquods, 0.62 percent organic matter, CEC 6.24 meq/100 g, 95 percent sand, 5 percent silt). Terrain is flat to gently rolling. Forests are slash pine (*Pinus elliotii* Engelm.) and loblolly pine (*Pinus taeda* L.) with understory of predominantly palmetto [*Serenoa repens* (Bartram) Small], gallberry [*Ilex glabra* (L.) Gray], low panicum grasses (*Panicum* spp.), wiregrass (*Aristida stricta* Michx.), and bluestem grasses (*Andropogon* spp.). Although flatwoods planting beds are often weed-free at time of planting, colonization by weeds occurs rapidly in the first growing season.

Two watersheds (treated, WS 4, and control, WS 6) were constructed by hydrologically isolating 4-6 ha plots with ditches and installing long-throated flumes at the lowest draining point (Figure 1). Topographic relief is on the order of 1 to 2 m. Streamflow in these flatwoods is typically ephemeral with no or low flow in March-April and October-November. The watersheds used in this study had very little flow after herbicide application in June due to the effects of a prolonged drought. Very high rainfall can involve submergence of the whole watershed and associated gauging structures. The site was clearcut harvested during the summer of 1984 and prepared for machine planting by chopping and bedding. Slash pine was planted in December 1984 at a spacing of 2 m within rows and 4 m between rows.

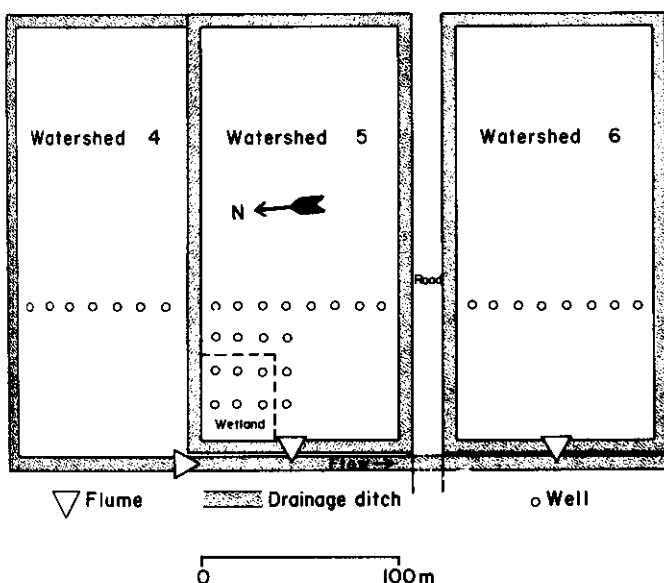


Figure 1. Site Layout Indicating Location of Watersheds, Sampling Wells, and Flumes.

Instrumentation

The study site was equipped with a standard rain gauge and a seven-day recording rain gauge. Both rain gauges were serviced weekly and precipitation was read directly from rain gauge charts.

Outflows from the watershed perimeter ditches were gauged with 60 cm long-throated flumes. Stage height was recorded by Belfort and Stevens analog water level recorders. Streamflow was derived from a stage-discharge calibration curve.

Seven shallow wells (5 cm diameter to a depth of 1.5 m) were installed 15 m apart in transects across each watershed. Wells were fitted with slotted PVC screen through most of their depth. Sampling inserts were installed to allow pumping of water from the bottom of each well with a minimum of common connections. The slotted-wells were capped, encased with an outer 10-cm capped casing driven 30 cm into the soil to prevent direct contamination. ISCO automatic water samplers were placed just upstream of the flumes for stormflow sampling.

Study Treatment

Herbicide was applied at the rate of 0.42 kg ha⁻¹ a.i. on June 13, 1985, without added surfactant, by a 4-nozzle, flat fan tractor-mounted system. The nozzles were held 60 cm off the ground surface. The spray

was applied at a rate of 200 L ha⁻¹ of well water carrier. At the time of treatment, wind was variable at 0 to 10 km hr⁻¹ with a temperature of 26.1 to 28.9°F and relative humidities of 57 to 76 percent. Buffer strips of 5 m were used along the perimeter ditches of the treated watershed. A control watershed was established 150 m to the south of the treated watershed.

Sampling

Water samples (1 liter) were collected by ISCO automatic samplers and by grab sampling. Automatic sampling by the ISCO's occurred hourly with 4-hr intervals composited into one sample. Grab samples were taken at the flume locations, and 30, 150, and 600 m downstream of the treated watershed. All water samples were stabilized with neutral phosphate buffer when collected and stored frozen until analyzed.

Coarse-fraction sediment was separated from water samples by decanting the supernatant water and suspended sediment. The resulting water sample was subsequently filtered and the filtrate was combined with the settled sediment. The combined sediments were air dried, weighed, and frozen until analyzed. Bottom sediments were collected at the flume and 30, 150, and 600 m downstream, and kept frozen until analyzed.

Chemical Analysis

All samples were analyzed by HPLC utilizing either a UV or photoconductivity detector. Water samples were analyzed by the method of Wells and Michael (1987) and sediment was analyzed after the soil method of Zahnow (1985). Detection limits were 1.0 mg m⁻³ for water and 0.020 mg kg⁻¹ for sediment.

Quality control (QC) samples consisted of blank and spiked samples from appropriate matrices. Material for these samples were collected from the control watersheds or as pretreatment samples from the treated watersheds. QC samples were interspersed among lab samples for extraction and analysis. Analytical standards were run as every fourth sample during analysis.

Freezer Stability Studies

Water samples collected from the study areas were spiked with analytical standard to make a sample

concentration of 100 mg m^{-3} sulfometuron methyl. The spiked samples were frozen with the field-collected samples, and analyzed periodically to determine whether any degradation had taken place during the storage process. Freezer stability samples were analyzed statistically by GLM and Tukey's test at the 0.05 probability level.

RESULTS AND DISCUSSION

Efficacy

Visual observations on this site indicated > 90 percent control of panicum grasses and broadleaved weeds with the spray application. Wiregrass was minimally affected. Gallberry, palmetto, blackberry (*Rubus* spp.), oaks (*Quercus* spp.), and chalky bluestem (*Andropogon capillipes*) were not affected by sulfometuron methyl as indicated in other studies (Neary, *et al.*, 1984). No herbicide-related pine mortality was observed. Drought-induced mortality amounted to 45 percent and was already evident at the time of the herbicide application.

Precipitation

There were seven storms yielding more than 25 mm of precipitation each during the study. Rain began within 24 hours of application (June 13, 1985) and again three days after treatment (DAT); a total of 54 mm of rain had fallen (Figure 2). The next significant rainfall occurred a month later in July (30 mm on the 10th, 46 mm on the 13th, 48 mm on the 14th, and 51 mm on the 31st). Rainfall in August was frequent, but not heavy until the end of the month.

Freezer Stability

The results of freezer stability studies are listed in Table 1. No changes were observed in spiked samples over the period of freezer storage. Most water samples were utilized within 12 weeks of collections, however, a few were stored for up to 32 weeks prior to analysis. All water samples were stored buffered to pH 7 and frozen. Because of the stability of sulfometuron methyl at pH 7, it is unlikely that any significant degradation occurred during the additional 18 weeks of storage for these few samples.

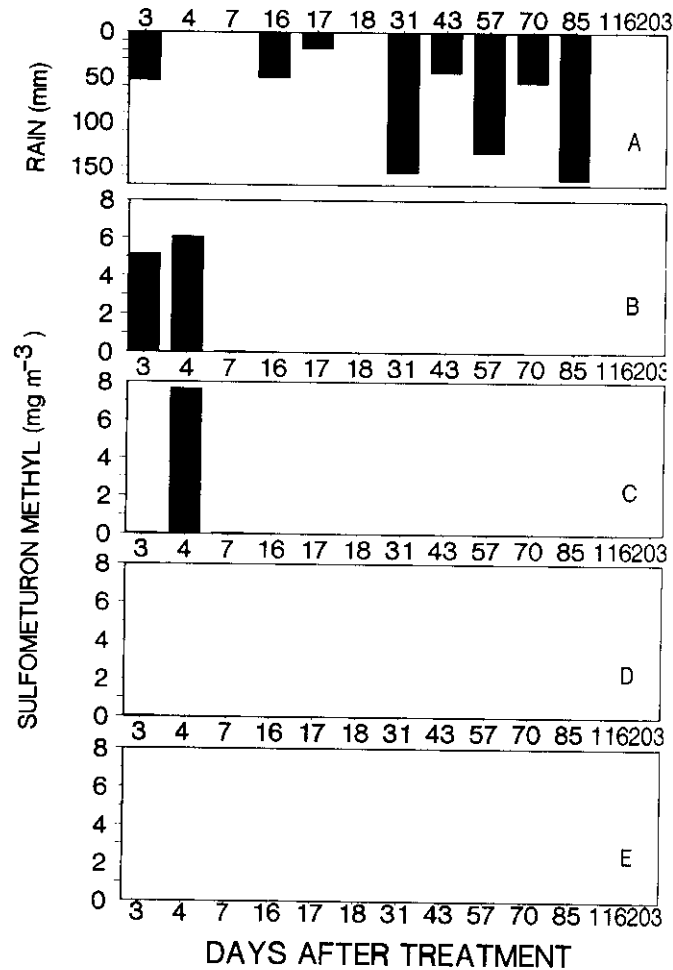


Figure 2. Rainfall (A) and Sulfometuron Methyl Residues in Streamflow at the WS 4 Flume (B), and 30 (C), 150 (D), and 600 m (E) downstream.

TABLE 1. Freezer Study of the Stability of Sulfometuron Methyl in Spiked Solutions Made With Pretreatment Water Collected from the Sprayed Site.

Time (weeks)	Average Recovery of Spike (percent)	Standard Deviation (percent)	Sample Size
0	94	3.3	4
2	86	10.2	4
4	89	3.8	4
6	92	8.8	4
12	91	3.4	4
14	92	1.1	3

Streamflow Residues

Sustained streamflow did not begin until about 20 DAT due to droughty conditions earlier in the year (Figure 2). Prior to 20 DAT, intermittent flow occurred. During this period, any sulfometuron methyl residues on vegetation, litter, or bare mineral soil surfaces would have been subjected to hydrolysis, adsorption, and microbial degradation.

A total of 44 grab samples of baseflow were collected at the flume, measuring flow from the treated site during the period between treatment and 203 DAT. Of these, only three contained quantifiable residues of sulfometuron methyl (Figure 3b). The maximum concentration observed in these samples was 6 mg m^{-3} (DAT 4). An additional four samples contained trace residues ($< 1.0 \text{ mg m}^{-3}$ but too low to quantify). After DAT 7, no detectable residues of sulfometuron methyl were measured in grab samples of streamflow at the flume. Thirty samples collected from the flume of the control watershed during the same time period did not contain sulfometuron methyl. These results are very similar to those reported by Bush, *et al.* (1988), for triclopyr [(3,5,6-trichloro-2-pyridinyl)oxy acetic acid] movement in streamflow from Lower Coastal Plain flatwoods watersheds.

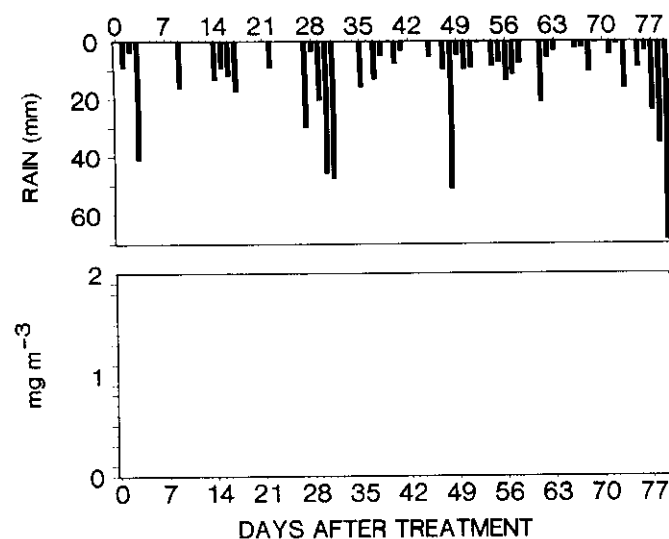


Figure 3. Sulfometuron Methyl Residues in Stormflow.

An additional 30 grab samples were collected downstream of the treated watershed. One sample contained 7 mg m^{-3} of sulfometuron methyl, two samples contained trace levels between 3 and 7 DAT at 30 m downstream (Figure 3c). One sample collected 150 m downstream on 3 DAT had a trace level of the herbicide (Figure 3d), and none of the samples collected 600 m downstream contained sulfometuron methyl (Figure 2e). Thus, there was no significant downstream movement of sulfometuron methyl.

Stormflow sampling was conducted during the first three months of the study. Four major rainfall periods occurred (June 14-16, June 27-30, July 30-August 3, and August 29-31). Each storm lasted more than one day and resulted in periods of significant streamflow. A total of 49 samples were collected during these four periods and were analyzed for sulfometuron methyl content (Figure 4). None of these stormflow samples contained detectable sulfometuron methyl residues. The second and fourth storms were large enough to saturate the soil and produce substantial surface runoff. Sulfometuron methyl was not detectable in runoff due to either large dilution in the stormflow, degradation, or sufficient retention of sulfometuron methyl on the treated site.

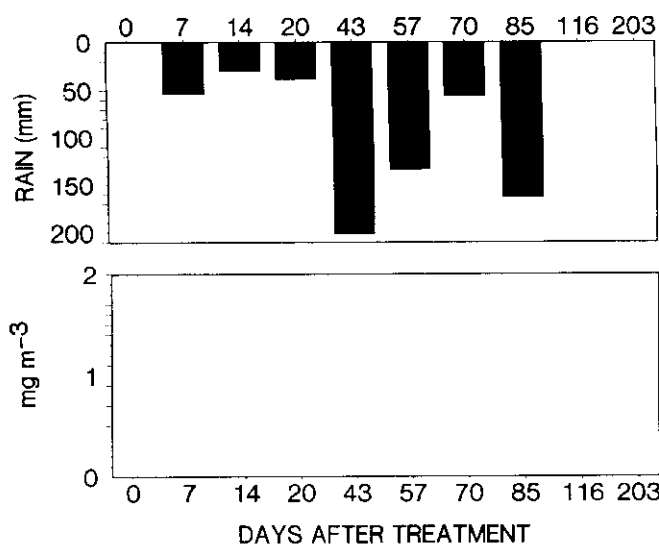


Figure 4. Sulfometuron Methyl Residues in Shallow Ground Water of Coastal Plain Flatwoods.

The peak sulfometuron methyl concentration (7 mg m^{-3}) measured in streamflow was 1,785 times lower than the 96 hr LC_{50} for bluegill sunfish, and 14 times the concentrations needed to affect hydrilla. Herbicide levels were seven-fold higher than those needed to reduce Eurasian watermilfoil growth, but they did not persist beyond three days.

Ground Water Residues

Monitoring wells were installed in the sulfometuron methyl treated and untreated control watersheds to determine if herbicide residues could move into shallow ground water. In flatwoods Spodosols, ground water is usually perched above an argillic horizon which occurs at a depth of 1.0 to 1.5 m below the surface (Comerford and Van Rees, 1985). This ground water has the highest hazard of contamination by herbicides since it is on-site and close to the surface. Such ground water is usually not used as water supply since it is ephemeral. Deeper secondary aquifers of unconsolidated sand, confined by clay seams, and the much deeper regional carbonate Floridan aquifer are the normal water supply aquifers. Pollution of the shallow aquifer commonly found in Coastal Plain flatwoods, however, is a good index to measure potentials for deeper aquifer contamination.

No samples were collected before 5 DAT due to low rainfall. Sixty-three ground water samples were collected between 5 and 213 DAT at various intervals. Sulfometuron methyl was not detected in the surface unconfined ground water aquifer at any time during the study. This was in spite of above normal precipitation in the latter half of June and all of July. The lack of any sulfometuron methyl in ground water is most likely due to rapid hydrolysis in the acidic Haplaquod soils. The soil A horizon averages pH 4.0. In those conditions sulfometuron methyl hydrolyzes rapidly. The hydrolytic half-life of sulfometuron methyl at pH 4.5 is approximately two weeks.

Sediment

Sulfometuron methyl was not detected in any sediment samples from either the treated or control watersheds. The low concentration in herbicide in solution in streamflow and the tendency for rapid breakdown in acidic drainage water created conditions that were not conducive for sulfometuron methyl transport in a sediment-sorbed phase. In addition, sediment movement in Coastal Plain flatwoods is usually minimal due to low relief (Riekerk, 1985).

SUMMARY AND CONCLUSIONS

Sulfometuron methyl residues were present in streamflow but were intermittent, at very low levels, and did not persist beyond 7 DAT. A small streamside management zone (5 m) was used for the ground-system application. Sulfometuron methyl was detected in very few samples (10 of 185 total samples) in the first storm between 3 and 7 DAT at a concentration of 7 mg m^{-3} or less. The most distant point downstream at which sulfometuron methyl was detected was 150 m (trace level). Residues of the herbicide were not detected in the water table $< 1.5 \text{ m}$ below the ground surface at any time. Most of the off-site movement occurred with the first two to three storm events. This is consistent with the findings of other researchers who report up to 90 percent of observed off-site movement occurs with the first storm events following application (Wauchope, 1978; Wauchope and Leonard, 1980).

The concentrations measured in stormflow compare favorably with those for other modern forestry herbicides applied at similar rates (Neary, 1986). Sampling intensity for water in this study was greater than that for most similar studies reported in the literature and therefore there was a high probability of detecting any residues. The extremely small number of water samples containing measurable residues of sulfometuron methyl in this study indicate very little off-site movement relative to other herbicides. Sulfometuron methyl was not detected in any bottom or suspended sediment samples. Operational use of sulfometuron methyl in forests of the Lower Coastal Plain of the Southeast has a minimal impact on water resources.

These results indicate that due to the low levels of sulfometuron methyl in stormflow within seven days of herbicide application, absence of residues in streamflow after seven days, absence of residues in the shallow water table, and the low toxicity implications ($> 1,785$ times lower than the LC_{50} for bluegill sunfish), sulfometuron methyl used in Coastal Plain flatwoods forestry has a very low potential for contaminating surface waters or regional ground water aquifers, or affecting aquatic organisms.

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